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1. Your reference

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2. Patent application number
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28 SEP 1999

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

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Patents ADP number *(if you know it)*

7435423001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

A Method of Processing a Polymer Layer

5. Name of your agent *(if you have one)*

Wynne-Jones, Laine & James

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Cheltenham
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Patents ADP number *(if you know it)*

1792001

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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
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Yes

A Method of Processing a Polymer Layer

This invention relates to a method of processing a polymer layer, such as a short chain polymer layer, including Si-C bonds and in particular for processing low dielectric constant films of the type, for example, that are used as insulating layers on semiconductor wafers.

The pressure to produce semiconductor wafers with high device densities and high speeds has led to a search for low dielectric constant films for use as insulating layers in semiconductor devices. Such layers can be either spun on or deposited using, for example, chemical vapour deposition process. The layer is then usually heated to harden it. Recent work has been particularly directed to films consisting of polymer layers including Si-C bonds and the applicant's International Patent Application WO 98/08249 describes, by way of example, such a process for depositing such a film.

The reduction in dielectric constant in such films seems to derive from a decreased density of film, possibly due to a disruption of the lattice by the carbon atoms present in the film.

The dielectric material forms or is deposited upon the wafer as a short chain polymer that is further polymerised and hardened by heating to between 400° and

500°C, typically in a nitrogen atmosphere of between 30 mTorr and 20 Torr and more generally in the absence of oxygen at any convenient pressure.

It has become apparent, however, that at least some films of this sort are susceptible to cracking, particularly at the wafer edge and an illustration of this is shown in Figure 1. Typically such cracking begins to occur at a nominal film thickness of about 5000-6000 Å. The cause seems in part to be due to a dramatic increase in film thickness within 1mm of the wafer edge. Figure 2 shows the profile in this respect. The cracking appears only to occur following exposure to atmosphere and aggressively travels in towards the centre over a period of about 24 hours. The rate of cracking can be delayed by keeping the wafers in vacuum, but eventually they do crack when exposed to atmosphere.

The present invention consists in a method of processing a polymer layer including Si-C bonds including the steps of heating the layer to desorb moisture and harden the layer and exposing the layer to a plasma during the heating process.

Usually the deposited polymer layer comprising a short chain polymer, the heating further polymerising the layer.

It is particularly preferred that the plasma is a hydrogen plasma, but it is believed that a plasma based on oxygen getters may be particularly appropriate. It is preferred that the plasma is present throughout the heating stage.

The plasma may be maintained by the wafer support RF driven electrode on which the layer is supported e.g. indirectly on a semiconductor wafer reactor electrode (sometimes known as Reactive Ion Etch (RIE) mode even if no etching occurs); by a capacitively coupled RF electrode spaced from the wafer (often referred to as a "diode configuration"; or by an inductively coupled arrangement (typically known as inductively coupled plasma (ICP)). In addition a combination of ICP and RIE can be run. In any of these cases, for the purposes of this invention the power supplied to the plasma may be of the order of between 400 and 750 watts the RF power required depending in part at what temperature the treatment of the layer takes place. Thus usually the wafer will be supported on a platen heated to a temperature of the order of between 350°C and 500°C.

In a particularly preferred arrangement the method has the following characteristics:

(1) The plasma is maintained by an RF power source connected to a platen on which the wafer is supported and the power supply provides substantially 600 watts.

(2) The plasma is a hydrogen plasma;

(3) The platen is heated to between 400°C and 500°C; and

(4) The heating step lasts for substantially 3 minutes.

In any of the above methods the dielectric constant of the processed layer is preferably below 3.

The layer may typically be an insulating layer on the semiconductor wafer.

Although the invention has been defined above, it is to be understood it includes any inventive combination of the features set out above or in the following description.

The invention may be performed in various ways and a specific embodiment will now be described by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a micrograph taken by an optical microscope of the edge of a wafer showing cracking of the

layer after exposure to atmosphere, the layer having been processed in the prior art manner.

Figure 2 is a graph demonstrating the thickness profile of a low k film;

Figure 3 illustrates k values resulting from various experiments;

Figure 4 is an equivalent graph for further process conditions;

Figure 5 shows Fourier Transform Infra Red (FTIR) data gathered from a central sample; and

Figure 6 shows FTIR data for a sample prepared in accordance with an embodiment of the invention.

Experiments were run to monitor both cracking and k (dielectric constant) values. Each property was also checked with time. The k values were measured on low resistivity silicon MOS structures and the cracking was monitored by optical microscope inspection under dark field illumination.

The deposition of the low k film onto silicon wafers was carried out in a standard chemical vapour deposition process with the following characteristics:

Methyl silane flow	100 sccm
Hydrogen peroxide	0.5 g/min
Pressure	1000 mTorr
Platen temperature	2°C
Showerhead temperature	100°C

As a first step, the thus deposited short-chain polymer layer was then subjected to the standard heat treatment, but this time with a coincident plasma. Various plasma treatments including hydrogen, argon, nitrogen, nitrous oxide and oxygen were run. Some benefit on cracking was observed which encouraged further experiments combining higher temperatures of heat treatment with various configurations of applied plasma power.

As has been discussed above, these plasma modes comprise the following:

(1) RIE

(2) Diode

(3) ICP

(4) ICP and RIE in combination.

Initially, hydrogen plasmas were run in RIE and ICP, both separately and combined, at temperatures of 400°C, 450°C and 500°C for three minutes and these were compared to an argon run in diode mode at 400°C.

The results of these experiments show that a reduction in cracking could be achieved and therefore further trials were carried out at higher temperatures in diode mode.

These further experiments used a hydrogen plasma with a nominal platen temperature of 500°C using a 13.56MHz power supply although, in the absence of the plasma, the wafer temperature is estimated to reach approximately 375°C due to poor thermal coupling at low pressures and in the absence of wafer clamping. Wafer temperatures whilst a plasma is running, would be expected to be higher. Difficulties were experienced in obtaining meaningful experimental measurements of actual wafer temperatures due to RF interference on thermocouples.

The typical process conditions using a hydrogen plasma were as follows:

Diode mode

R.F. Power	1000 W
R.F. Frequency	13.56 MHz
Hydrogen flow	1000 sccm
Pressure	4 Torr
Platen Temperature	500°C (Wafer temperature unknown but >375°C)
Spacing	10mm
Time	180 seconds

ICP and RIE modes:

	ICP mode	RIE mode'	ICP+RIE
R.F.Power ICP	500W	-	-
R.F.Power Platen	-	600W	-
R.F.Power ICP/Platen	-	-	500/250
Pressure	4m Torr	450 mTorr	4 Torr
Platen Temperature	400-500°C	350-500°C	400-500°C
Time	60-300 secs	60-300 secs	60-300secs

The preferred process was run at 350°C or 400°C for three minutes. Argon was also used but hydrogen was preferred. Hydrogen produced DC bias levels of 475V against 260V with argon.

In addition control experiments were run using a typical heat only process and the two conditions used are set out below.

	Step 1	Step 2
Platen temperature (wafer temperature)	500°C(~150°C)	500°C(~460°C)
Pressure	30 mTorr	10 Torr
Time	60 seconds	300 seconds

The results of many of these experiments are illustrated in Figure 3. This shows the k value obtained for various process temperatures, excitation modes and time periods. That for the 500° temperature/ICP and RIE combined may show a measurement error, but alternatively it may be indicative of some irreversible change taking place if the film exceeds a critical temperature.

Each result represents a single experiment and a subsequent k value measurement.

Crack tests were carried out on approximately 7,000 Å films. The RIE only treatments showed no cracking, whilst the controls (heat treatment only) cracked to 25mm from the edge of the wafer. There was minimal cracking up to approximately 0.25mm from the edge of the ICP and combined

ICP and RIE treatments, although there was no significant trend with platen temperatures in the range 400°C to 500°C. The RIE alone process also achieved particularly desirable k values and so, from the work done to date, this would appear to be the preferred process although the higher k values may be acceptable for many wafer configurations.

Figure 4 shows a further experiment using RIE modes of treatment mainly for hydrogen plasmas but with variations in the time and temperature combinations. The third pair of points from the right were obtained with an argon plasma. The controls were prepared as before. The measurement bars for the k values indicate that obtained shortly after treatment and that obtained 48 hours after the treatment.

The degree of cracking was worse for argon and for the 350°C/60s treatment. These experiments showed cracking extending approximately 0.33mm in from the wafer edge for approximately 7000 Å film, but it will be appreciated that these results are still noticeably better than for heat treatment alone. The other results showed cracking was not seen until almost 9000 Å film thickness occurred and the best process seems to lie for a film between 8000 and 9000 Å. Note that these are nominal layer thicknesses across the majority of the wafer. Cracking

takes place in a part of the layer much thicker than this nominal thickness e.g. at the edge of the wafer as illustrated in Figure 2.

Some further experiments have been run in diode mode which suggests that comparable benefits to RIE can be obtained, but the plasmas were run at a much higher pressure (4 Torr) and much higher powers (1000 watts). This may significantly affect the wafer temperature and consideration may have to be given to the question of thermal budget.

Figure 5 shows FTIR data gathered with the control process whilst Figure 6 shows similar data from a hydrogen plasma diode mode. The heat only proves results in a final wafer temperature of approximately 460°C the wafer temperature of the hydrogen plasma treated wafer is not definitely known but must be greater than 375°C as this is the wafer temperature achieved without plasma (all other process conditions remaining the same). It is thus clear that the hydrogen plasma treatment may result in a different wafer temperature to that of the prior art process of the control and thus affects the layer treatment. It is also believed that the plasma acts upon the layer not simply as a heat source. There are obvious differences resulting from the hydrogen plasma treatment.

Figure 6 shows reduced C-H, Si-H, $Si-CH_3$ and $Si-O(Si_2O_3)$ peaks. From previous experience the Applicants would have expected that such a variation would have yielded higher k values however the k values of the two examples shown are 2.84 and 2.77 respectively.

The following table shows the results of the k values and cracking distances for diode mode plasma treatment as set out above.

Treatment Temperature	Thickness after treatment	K value after treatment	K value after 24 hours	Cracking (distance from edge)
200	8819	2.86	3.05	5.00 mm
300	8382	-	-	2.00 mm
400	7871	2.76	2.79	0.75 mm
500	7731	2.76	2.77	None

Thus the hydrogen plasma treatment significantly changes the film structure, as shown by the FTIR. Whilst it is difficult to reconcile these changes with the fact that the k value remains low, this reduction in carbon and hydrogen content may make these films more convenient for use in semiconductor manufacture. The process is thus of value not simply to avoid the cracking of thick (greater than 7000-Å) polymer layers containing Si-C bonds.

CLAIMS

1. A method of processing a polymer layer including Si-C bonds including the steps of heating the layer to desorb moisture and harden the layer and exposing the layer to a plasma during the heating process.

2. A method as claimed in Claim 1 wherein the plasma is a hydrogen plasma.

3. A method as claimed in Claim 1 wherein the plasma is present throughout the heating stage.

4. A method as claimed in any one of the preceding claims where the layer is supported on an electrode and the plasma is at least partially maintained by an RF power source connected to the electrode.

5. A method as claimed in Claim 4 wherein the power source is between 400 and 750 watts.

6. A method as claimed in any one of claims 1 to 3 wherein the plasma is at least partially maintained by an RF power source feeding an electrode spaced from the layer.

7. A method as claimed in Claim 6 wherein the power is supplied between 400 and 750 watts.

8. A method as claimed in any one of Claims 1 to 5 wherein the plasma is at least partially maintained by an inductively coupled power source.

9. A method as claimed in Claim 8 wherein the power supplied is between 400 and 750 watts.

10. A method as claimed in any one of the preceding claims wherein the heating step lasts for between 2 and 4 minutes.

11. A method as claimed in Claim 10 wherein the heating step lasts for 3 minutes.

12. A method as claimed in any one of the preceding claims wherein the layer is supported as a platen heated to between 350°C and 500°C.

13. A method as claimed in Claim 1 wherein:

(1) the plasma is maintained by an RF power source connected to a platen on which the layer is supported and the power source provides substantially 600 watts;

(2) the plasma is a hydrogen plasma;

(3) the platen is heated to between 400°C and 500°C; and

(4) the heating step lasts for substantially 3 minutes.

14. A method as claimed in any one of the preceding claims wherein the dielectric constant of the processed layer is below 3.00.

15. A method as claimed in any one of the preceding claims wherein the layer is an insulating layer on a semiconductor wafer.

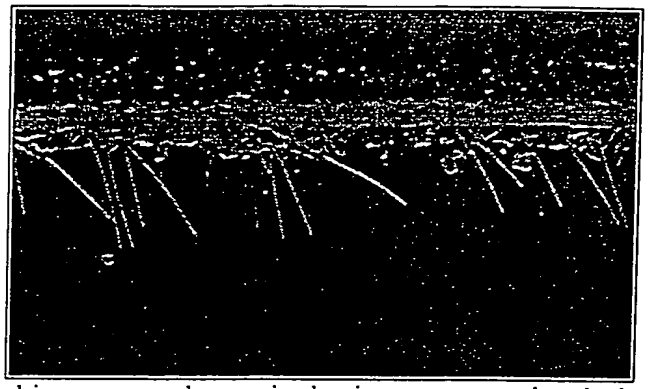


Figure 1. Edge cracking as seen by optical microscope under dark field illumination.

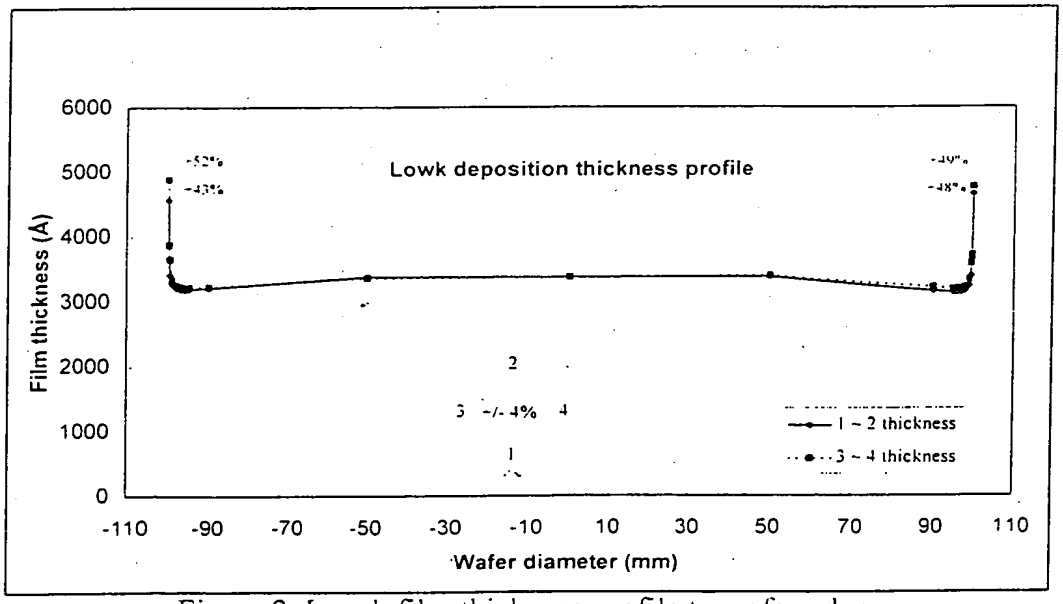
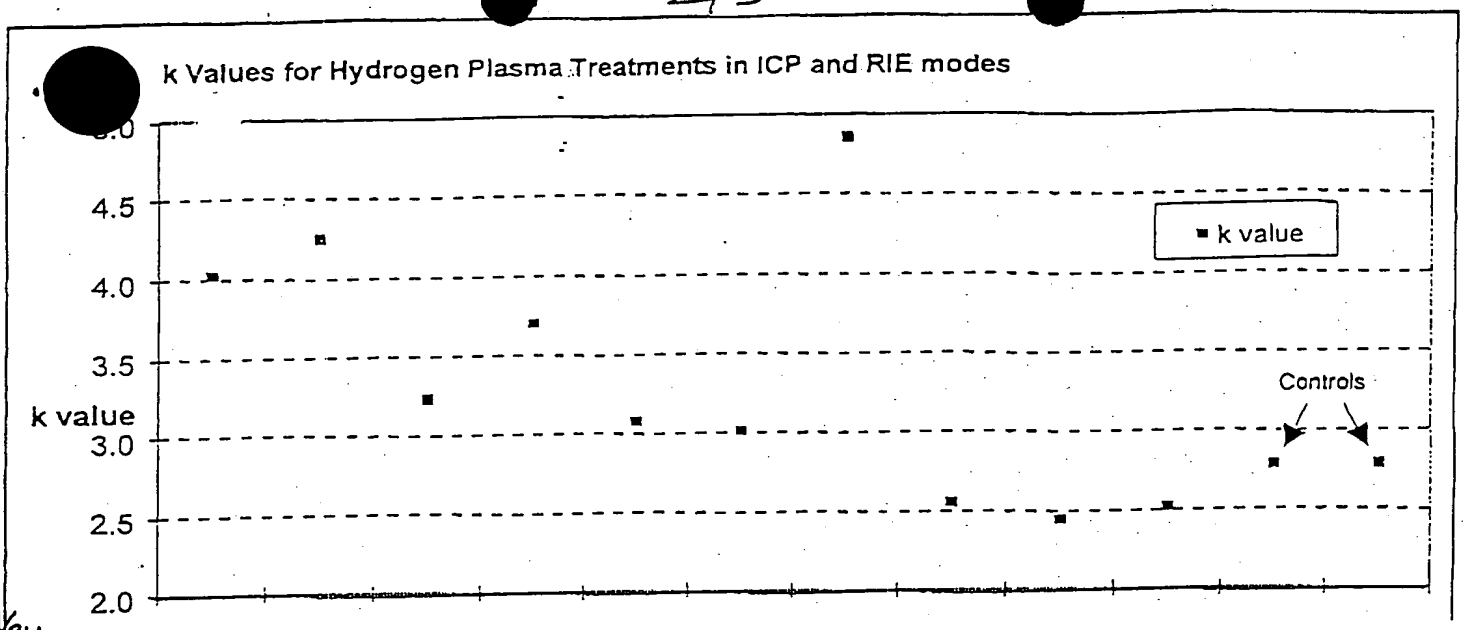
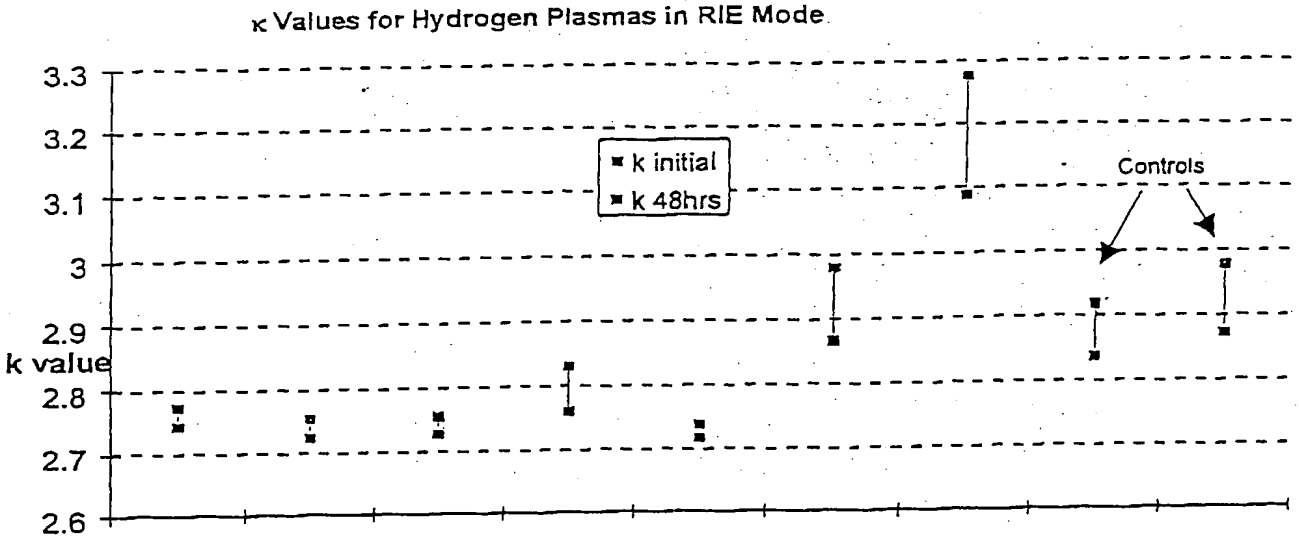


Figure 2. Low k film thickness profile to wafer edge.



Taken										
Temp °C	400	450	450	500	400	450	500	400	450	500
ICP Watts	500	500	500	500	500	500	500			
RIE Watts					250	250	250	600	600	600
Time mins	3	3	5	3	3	3	3	3	3	3

FIG 3



Temp °C	400	400	400	400	350	350	400
RIE Watts	600	600	600	600	600	600	600
Time mins	3	3	2	1	3	1	3
Gas	H_2	H_2	H_2	H_2	H_2	H_2	Ar

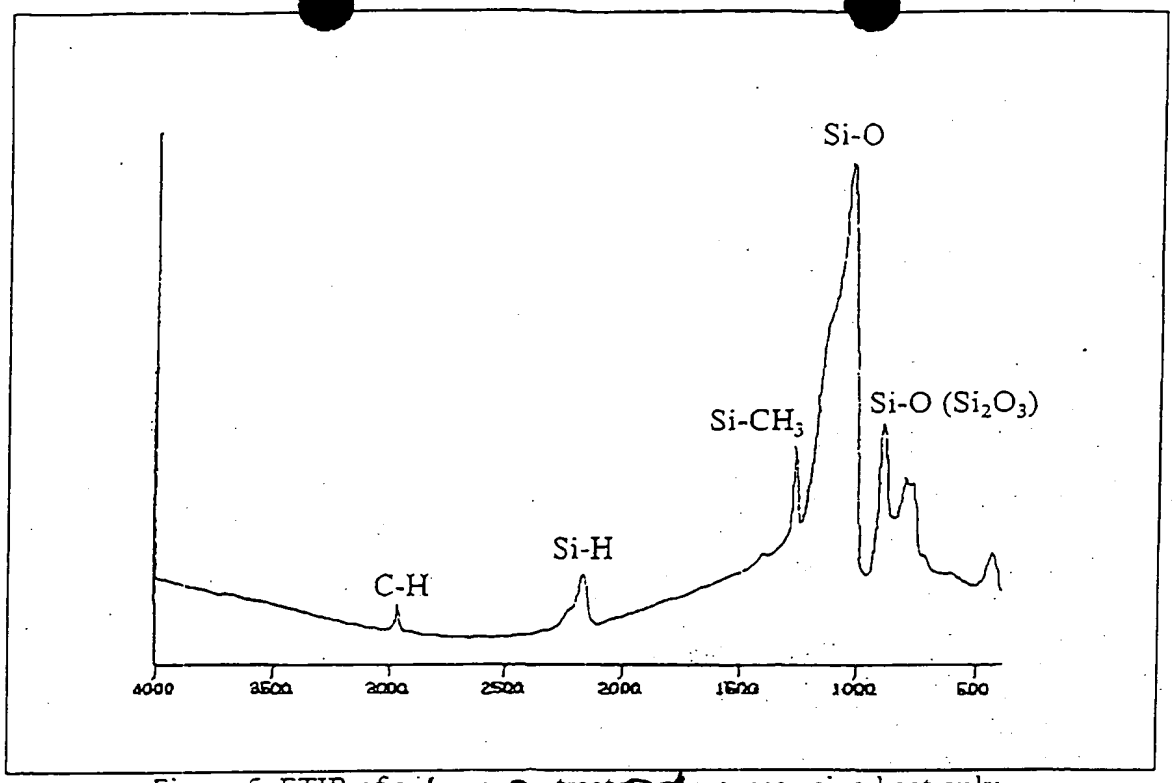


Figure 5. FTIR of a layer treated using heat only.

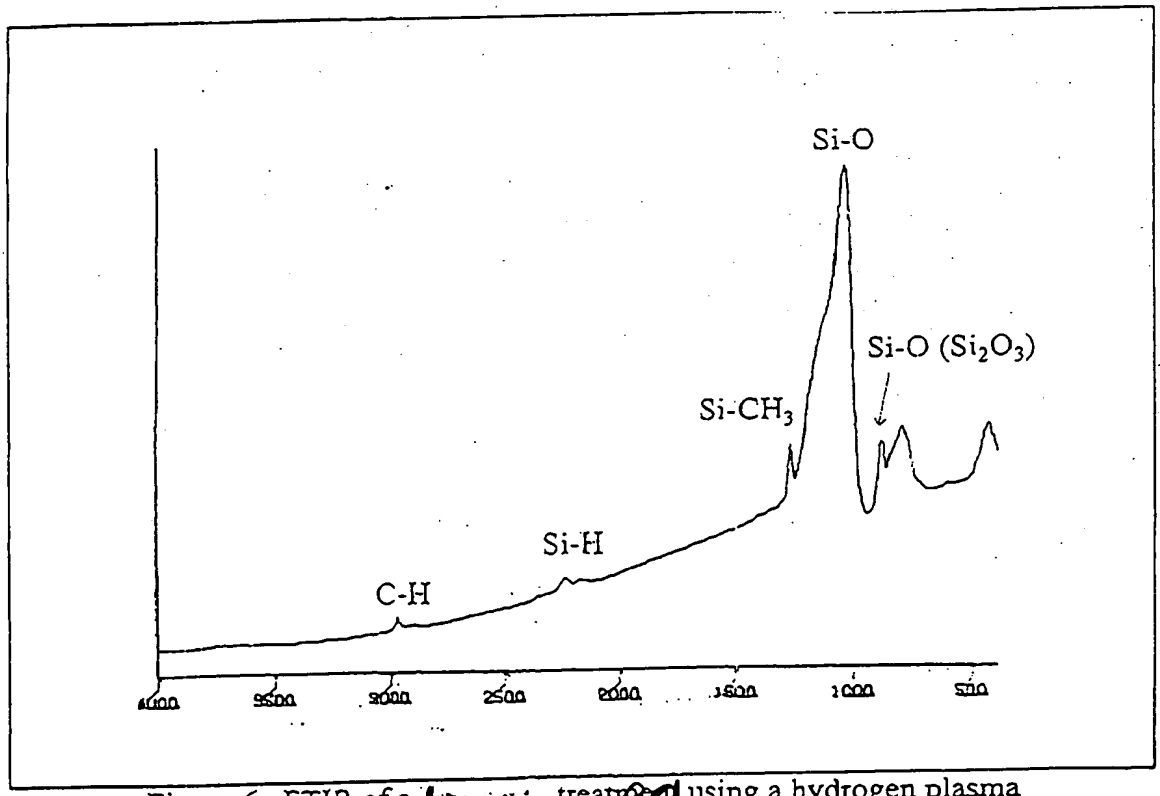


Figure 6. FTIR of a layer treated using a hydrogen plasma

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